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14. ABSTRACT
Chemical dynamics simulations were performed to obtain atomic-level understandings of chemical reaction and energy transfer processes in three research areas of importance to AFOSR: (1) collision energy transfer to surfaces is important for spacecraft in low-earth orbit (LEO) and excellent agreement with experiment was found in simulations of energy transfer in collisions of Ne atoms and CO_2 molecules with self-assembled monolayer surfaces. The simulations provide an atomistic picture of the energy transfer dynamics; (2) to understand the atomic-level dynamics of hypergolic ignition, mechanisms were investigated for the interaction of two methylhydrazyl ($N2H2CH3$) radicals, which react by either recombination or H-atom abstraction, ultimately forming $N2$ in highly exothermic pathways; and (3) a model was developed to study the rate of heat transfer from a hot gold surface to the atoms of a self-assembled monolayer, to simulate the experimental study of Dlott and co-workers. The simulation results are in excellent agreement with experiment and provide an atomic-level picture of the heat transfer.

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SUMMARY

Our accomplishments in chemical dynamics simulations are in four different areas: (1) collision energy transfer to the polymer surface of spacecraft is important when the spacecraft are in low-earth orbit (LEO). To obtain an atomic-level understanding of the relationships between the efficiency of this collision energy transfer and the projectile and surface properties, we continued our studies of energy in collisions of rare gas atoms and small molecules with self-assembled monolayer (SAM) surfaces; *J. Phys. Chem. C* **112**, 20340 (2008) and *J. Phys. Chem. A* **113**, 3850 (2009); (2) to understand the atomic-level dynamics of hypergolic ignition, the PES has been investigated for the interaction of two methylhydrazyl ($N_2H_2CH_3\bullet$) radicals, which react by either recombination or H-atom abstraction, ultimately forming N_2 in highly exothermic pathways. A manuscript is in preparation describing our calculations; (3) a model was developed to study the rate of heat transfer from a gold surface to the atoms in a SAM to simulate the experimental study by Dlott and co-workers in *Science* **317**, 787 (2007). The initial simulation results were published in *Phys. Chem. Chem. Phys.* **12**, 4435 (2010). More recently we have studied the effect of the carbon chain length on the rate of heat transfer to the SAM and this work has been accepted for publication; *J. Phys. Chem. C* **115**, in press (2011). The results of the simulations are in excellent agreement with experiment and provide an atomic-level understanding of the heat transfer; and (4) DFT calculations were performed on the isolated ions in imidazolium ionic liquids to guide the assignment of the vibrational spectrum in the 0-200 cm-1 region to intermolecular and intramolecular vibrational modes of the liquid; *Chem. Phys. Lett.* **497**, 37 (2010).

REPORT

During this period of study we have used computational and theoretical chemistry to study four different research projects; (1) energy transfer in collisions of Ne atoms and CO_2 molecules with self-assembled monolayer (SAM) surfaces; (2) dynamics of energy release in hypergolic ignition involving monomethyl-hydrazine (MMH); (3) heat transfer between a metal surface and a hydrocarbon film, which is important for nano-devices; and

(4) DFT calculations of the vibrational spectrum of individual molecules in an ionic liquid to assist in assigning the experimental spectrum.

I. Energy Transfer in Collisions of Ne Atoms and CO_2 Molecules with Self-Assembled Monolayer (SAM) Surfaces

Investigations of energy transfer and collisional accommodation between a gas and liquid or polymer surface are of fundamental importance in acquiring a thorough comprehension of heterogeneous chemical phenomena at the molecular level. These studies are of practical importance for modeling collisional energy transfer to spacecraft in low-earth orbit (LEO). Chemical dynamics simulations were performed to study energy transfer in collisions of Ne atoms with liquid squalane and CO_2 molecules with a perfluorinated self-assembled monolayer, F-SAM, surface. A united-atom (UA) model was used for squalane and both explicit-atom (EA) and UA models were used for the F-SAM. A snapshot of a trajectory for EA/F-SAM system is shown below.
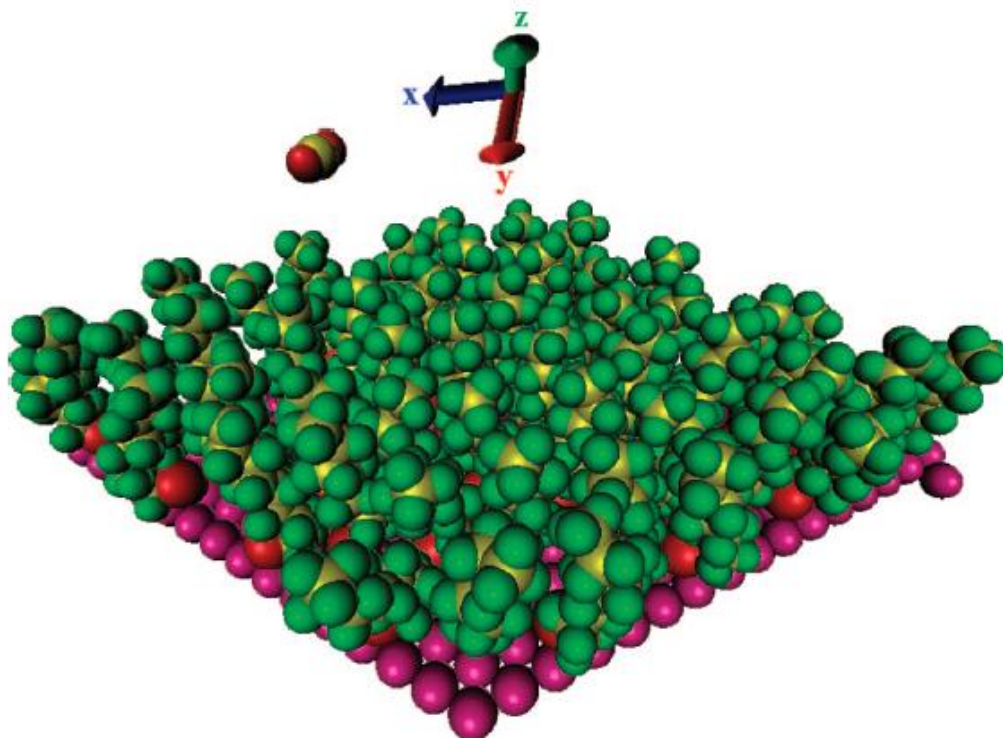

Figure 1. Snapshot of the EA model of the F-SAM surface after a collision with CO_2.

For the Ne + squalane study, the incident Ne atoms have short residence times on squalane, but the incident energy is dissipated efficiently, and more than 60% of the initial energy of the Ne atoms is transferred with three or more "kicks" on the surface. The calculated energy transfer efficiency is in excellent agreement with experiments by Nathanson and co-workers. A bimodal energy distribution is observed for both in-plane and out-of-plane scattering. Comparison with a previous study of Ne-atom scattering off a H-terminated SAM, H-SAM, shows that the energy transfer to squalane is less efficient than to the H-SAM, because flexible intermolecular couplings of the alkyl thiol chains of the H-SAM provide efficient dissipation channels to accommodate the incident Ne atom's energy.

Collisions of CO_2 with a F-SAM surface on gold were investigated by chemical dynamics simulations using both UA and EA models to represent the F-SAM. Of particular interest and for comparison with experiment by Nesbitt and co-workers, is the distribution of rotational energy, $P(J)$, transferred to CO2 by the collisions, As shown in the Figure 2 below, direct, penetrating, and physisorption trajectories were observed for the different collision energies E_i. The $P(J)$ distribution depends on both the collision energy and trajectory type. The agreement between the experimental and simulation $P(J)$ is especially good for the EA model. Calculations in which the mass of the F-atoms of the F-SAM are increased to those of H-atoms to represent a H-SAM, predict the observed experimental trend that less energy is transferred to the F-SAM as compared to the H-SAM. Significant differences were found between results obtained with the UA and EA models of the F-SAM. The UA surface leads to an enhancement of the energy transfer efficiency in comparison with the EA surface. The reason for this is the softer structure of the UA surface, which facilitates transfer from translation to inter-chain vibrational modes.
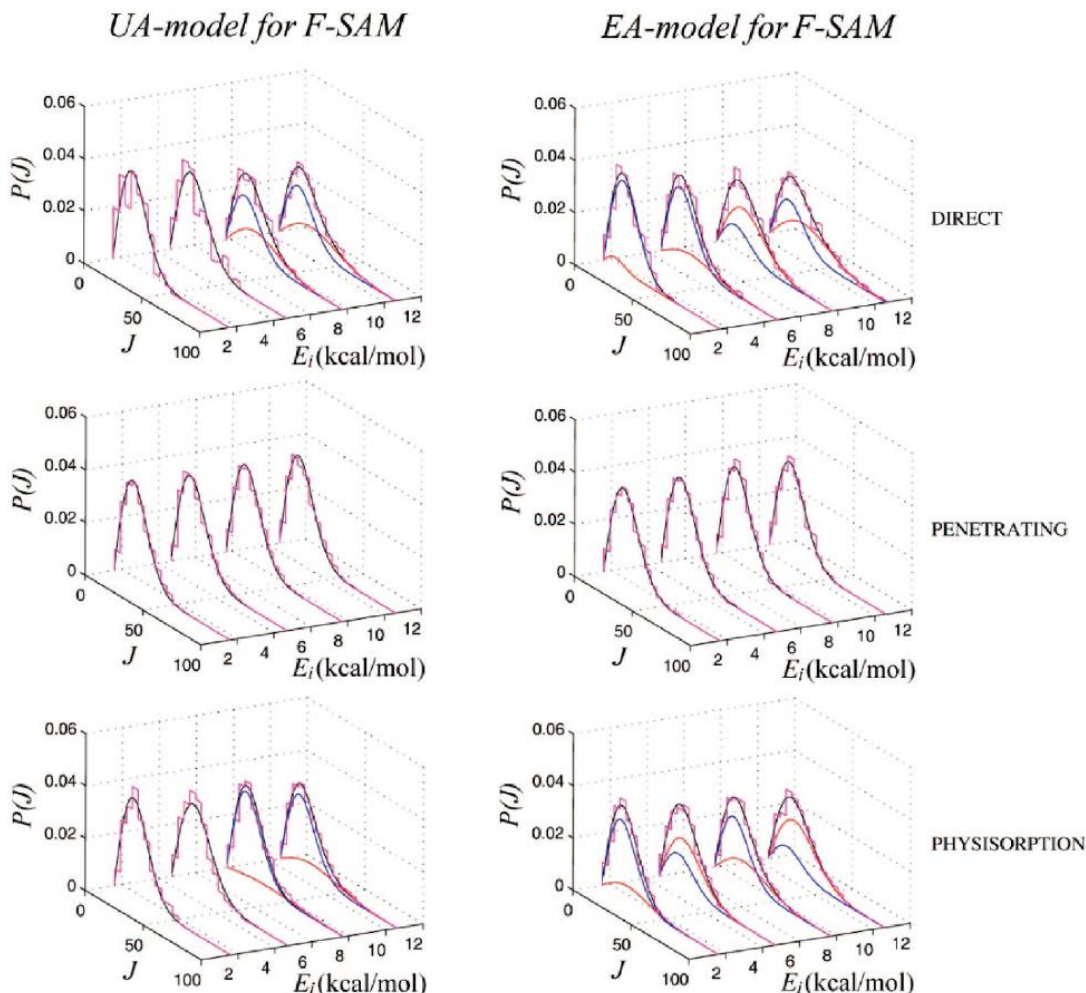
Figure 2. Distributions of the CO_2 rotational quantum number, for different trajectory types, as a function of the collision energy. The black lines are bimodal fits to the P(J), with the blue and red lines the low-temperature and high-temperature components, respectively.

II. Reactions of Methylhydrazyl Radicals Generated During the Reactions of Methylhydrazine and Nitrogen Tetraoxide

This research project is focused on the exploration on the possible reactions channels of radicals $CH_3NHNH\cdot$ and $CH_3N\cdot NH_2$ generated during the reaction of CH_3NHNH_2 and N_2O_4. The first stage of the study was to select the adequate level of theory, to represent the potential energy surface (PES) for the association of

methylhydrazyl radicals, the heterolytic dissociation channels of tetrazane isomers formed by the association of $CH_3NHNH\cdot$ and $CH_3N\cdot NH_2$ radicals, and to use in direct dynamics simulations. The second stage of the study, currently in progress, is an investigation of the heterolytic dissociation channels of methylhydrazyl radicals under an acidic environment, using the MSINDO-Venus program.

Selection of Adequate Level of Theory. Three methods were considered; i.e. UMP2, UDFT(B3LYP) and CASSCF. The method selected should describe the association of methylhydrazyl radicals (or equivalently, the homolytic dissociation of tetrazane) correctly, and should be feasible in a direct dynamics trajectory simulation. Among these methods, UB3LYP is the one satisfying these criteria and was selected as the level of theory for the study. The potential energy surface exploration and trajectory simulation are performed at UB3LYP/6-31G** level of theory.

Potential Energy Surface for Different Reaction Channels of Methyl Hydrazyl Radicals

Methylhydrazyl radicals may either associate to form dimethyltetrazane (DMTT), or undergo intermolecular hydrogen transfer. Association may form three different DMTT isomers 1,3_DMTT ($CH_3NHNHN(CH_3)NH_2$, 1,4-DMTT ($CH_3NHNHNHNHCH_3$) and 2,3-DMTT ($NH_2(CH_3)NHNH(CH_3)NH_2$), which are formed with 22.09, 25.81 and 23.44 kcal/mol excess energy, respectively. The accessibility of other heterolytic dissociation channels, in addition to the one back to the methylhydrazyl radicals, depends on the structure of tetrazane isomers and their energy barriers. For 2,3-DMTT, there are no fragmentation channels except the homolytic dissociation to form two $CH_3NHNH\cdot$ radicals.
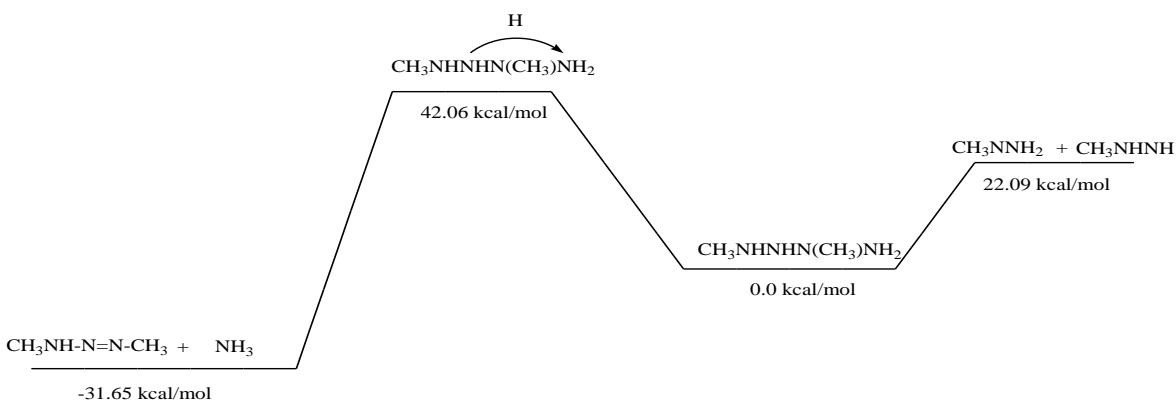

Figure 3. The potential energy surface for the dissociation of 1,3-DMTT

For 1,3- and 1,4-DMTT, other possible fragmentation pathways involve intramolecular hydrogen transfer, followed by the loss of the neutral closed-shell species NH_3 and CH_3NH_2, respectively, with energy barriers of 42 and 50 kcal/mol, respectively. The PES for 1,3 –DMTT is illustrated in Figure 3 above as an example.

The following intermolecular hydrogen transfer pathway also has been found for the methylhydrazyl radicals:

$$CH_3N\cdot NH_2 + CH_3NHNH\cdot \rightarrow CH_3NHN + CH_3NHNH_2$$
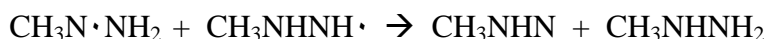
The formed nitriene (singlet) can undergo simultaneous intramolecular hydrogen migration and N-N cleavage, to form CH_4 and N_2. The PES is associated with two energy barriers, 14.6 and 45.3 kcal/mol, respectively, although the reaction is 82 kcal/mol exothermic.

Direct Dynamics Trajectory Simulations

Direct dynamics simulations are in progress in which the trajectories are initiated at the TS's on the potential energy surface. If interest is to determine the products formed and their energy partitioning.

Conclusion. Based on the completed research, we conclude that the methylhydrazyl radicals can recombine to form dimethyltetrazane. However, the excess energy owed by DMTT is not sufficient enough for the system to undergo other fragmentation channels. Therefore, our next step is to introduce the second component (HNO_2), to explore the fragmentation behavior of methylhydrazyl and its association product under acidic environment.

III. Heat Transfer Between a Metal Surface and a Hydrocarbon Film

Model non-equilibrium molecular dynamics (MD) simulations were performed for heat transfer from a hot Au {111} substrate to an alkylthiolate self-assembled monolayer (H-SAM) to assist in obtaining an atomic-level understanding of experiments by the Dana Dlott research group (*Science* **2007**, *317*, 787). Different models were considered to determine how they affect the heat transfer dynamics. They include temperature equilibrated (TE) and temperature gradient (TG) thermostat models for the Au(s) surface,

and soft and stiff S/Au(s) models for bonding of the S-atoms to the Au(s) surface. A detailed analysis of the non-equilibrium heat transfer at the heterogeneous interface was made. As shown in figure 3, there is a short time temperature gradient within the top layers of the Au(s) surface. The S-atoms heat rapidly, much faster than do the C-atoms in
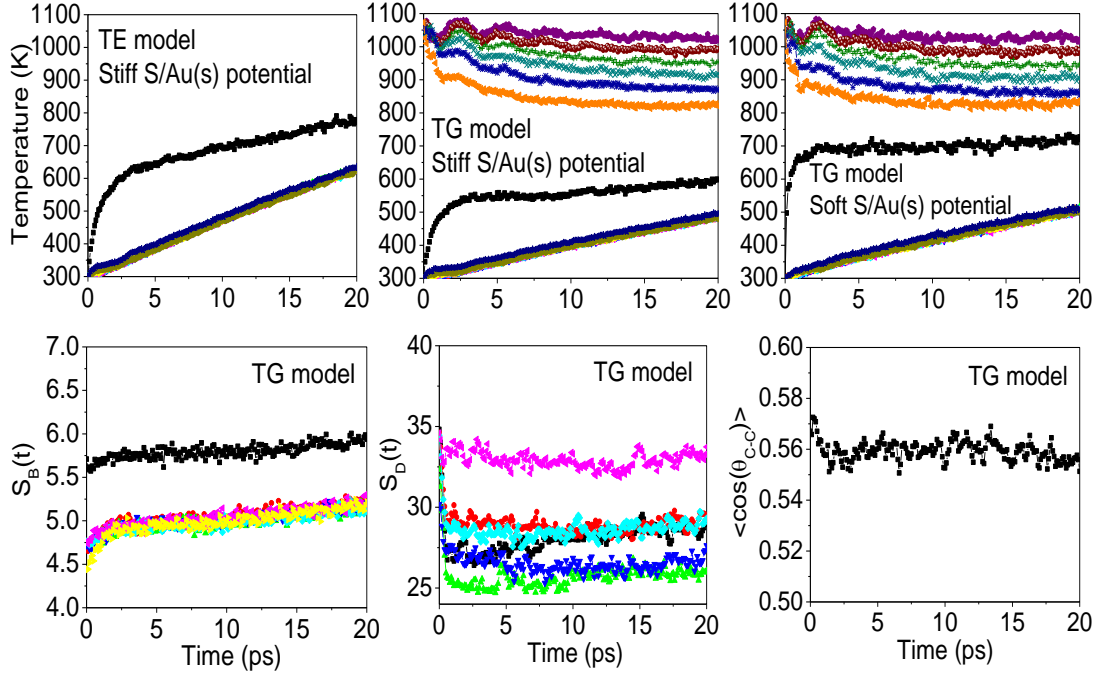

Figure 4. Short-time heat transfer and disorder dynamics. The top graphs give the temperatures of the different atomic layers of the H-SAM/Au(s) system versus time, for the TE and TG thermostats and the soft and stiff S/Au(s) potentials. For the TE thermostat the Au-layers are at 1073 K and their temperature is not shown. The temperatures of the six Au-layers, not coupled to the thermostat, are shown for the TG model. The warmest Au-layer is the most distant from the H-SAM and the coolest Au-layer closest. The temperature of the S-atom layer is given in black. The temperatures of the CH_2 and CH_3 layers are nearly identical and increase linearly with time. The bottom graphs give the disorder dynamics using the TG and stiff models. Shown are the disorders, Eq. (5), $S_B(t)$ for the S-C-C bend (black curve) six C-C-C bends (similar temperature dependence), and $S_D(t)$ for the dihedrals (starting at the terminal dihedral angle and proceeding to the S-C-C-C dihedral angle at the interface, the colors of the plots for the six dihedral angles are

purple, cyano, blue, green, red, and black). Also shown versus time is $<\cos\theta_{C-C}>$, the average value of $\cos\theta$ for the angles between all the terminal C-C bonds.

the alkylthiolate chains. A high thermal conductivity in the H-SAM, perpendicular to the interface, results in nearly identical temperatures for the CH_2 and CH_3 groups versus time. Thermal-induced disorder is analyzed for the Au(s) substrate, the S/Au(s) interface and the H-SAM. Before heat transfer occurs from the hot Au(s) substrate to the H-SAM, there is disorder at the S/Au(s) interface and within the alkylthiolate chains arising from heat–induced disorder near the surface of hot Au(s). The short-time rapid heating of the S-atoms enhances this disorder. The increasing disorder of H-SAM chains with time results from both disorder at the Au/S interface and heat transfer to the H-SAM chains. The increase disorder versus time is illustrated by the line density distribution functions plotted in Figure 4.
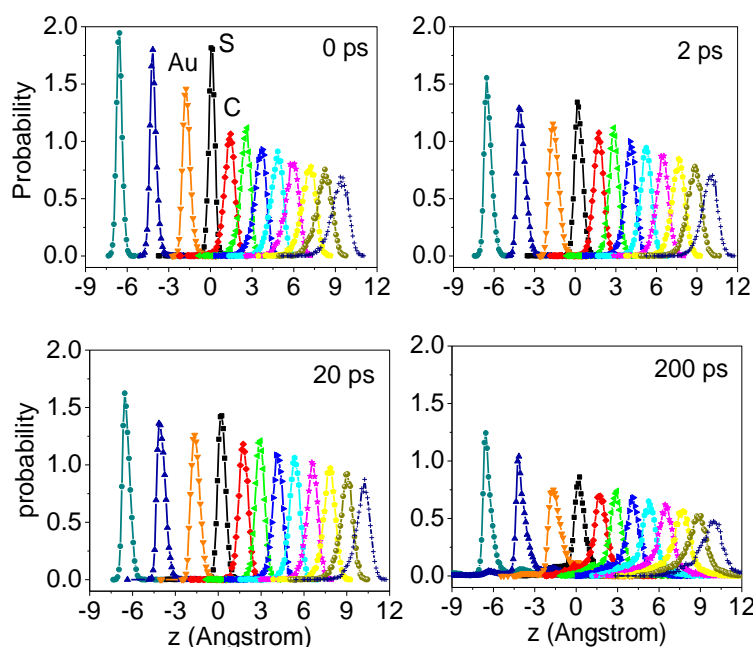

Figure 4. Line density distributions versus time for the Au-atoms of the top 3-layers, the S-atom layer and all C-atom layers.

The above simulations were performed for a H-SAM chain length of H-atoms. Simulations were also performed for heat transfer to H-SAM surfaces with carbon chain lengths of 10-20 carbon atoms; see Figure 5 below. Relaxation times for heat transfer are

extracted, compared with experiment and qualitative agreement is obtained. The same relaxation time is found from either the temperature of the H-SAM or the orientational disorder of the H-SAM versus time.
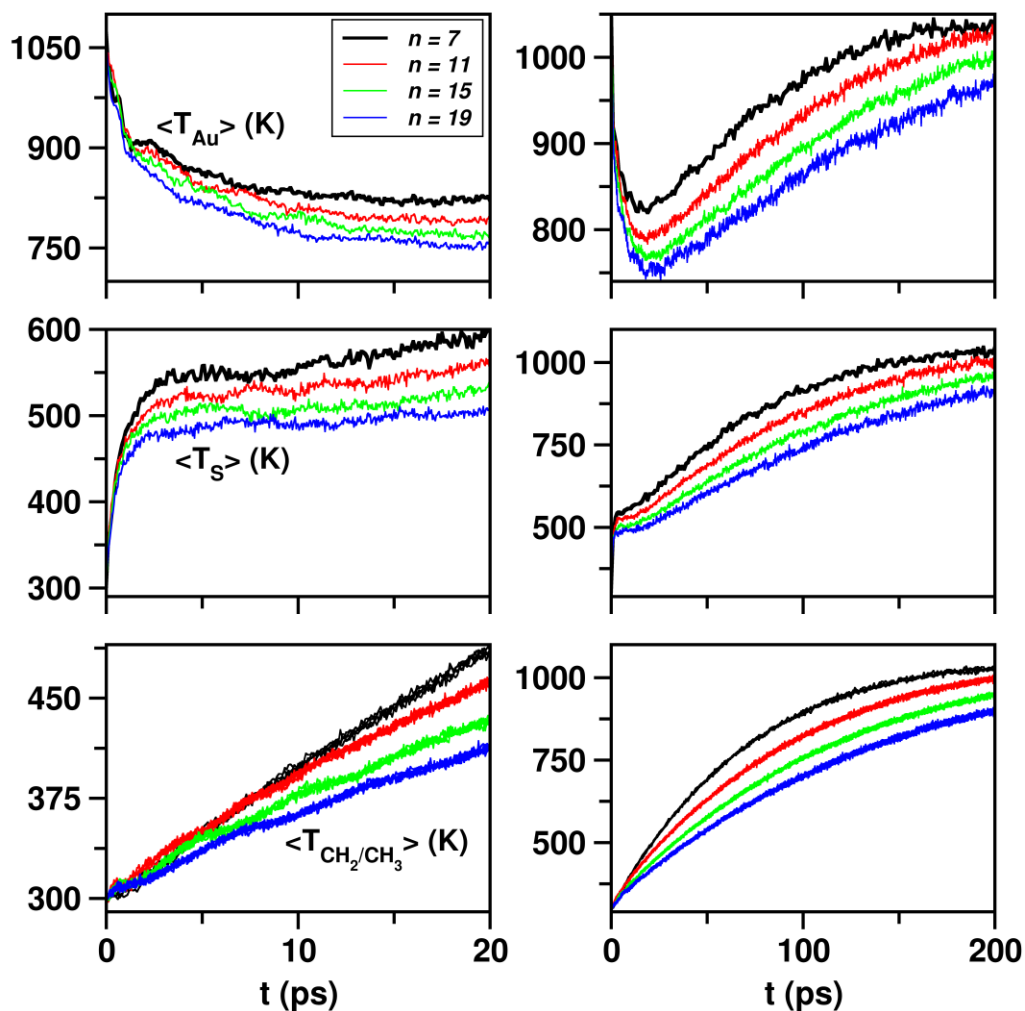

Figure 5. Short (left panels) and long (right panels) time heat transfer dynamics of the Au(s)/H-SAM system with different carbon chain lengths for the TG models. Top, middle and bottom panels show temperatures of the Au layer closest to the H-SAM system, the S layer, and the CH_2/CH_3 layers, respectively. The shorter chains heat up rapidly compared to the longer ones. The standard deviations in average values vary from 1-8 %.

Heat transport is important in the operation of mechanical and electronic devices, and its macroscopic understanding involves concepts such as heat diffusion by phonons and thermal conductivity. The work reported here shows that molecular dynamics simulations may be used to obtain an atomic-level understanding of this heat transfer.

IV. Low-Frequency Spectra of Imidazolium Ionic Liquids

DFT calculations were performed on the isolated ions in imidazolium ionic liquids to guide the assignment of the vibrational spectrum in the 0-200 cm-1 region to intermolecular and intramolecular vibrational modes of the liquid. The calculations allowed an interpretation of Raman spectra of the liquids.